

Formaldehyde-free bath for the electroless deposition of copper, method and use  
of polyethylene imines in formaldehyde-free baths

The invention relates to a formaldehyde-free bath for the electroless deposition of copper and a method and use of polyethylene imines in formaldehyde-free baths.

A multiplicity of reductive copper baths for the electroless deposition are known within prior art (for example disclosed in *Galvanotechnik* 80, 406 (1989) and US 4,695,505). Copper is conventionally reduced to metallic copper from a strongly alkaline copper solution by means of formaldehyde. The fundamental composition of such formaldehyde-containing baths has essentially not changed since approximately 1960. Apart from the reducing agent formaldehyde, the baths contain copper ions in free or complexed form and, as a rule, in addition also a stabilizer.

Operating these formaldehyde-containing baths is noticeably costly and elaborate as it requires large monitoring expenditures. Up to four regenerant solutions must partially be utilized in order to arrive at a satisfactory copper deposition while maintaining the nominal values of the substances contained in the bath. The reducing properties of the highly toxic formaldehyde can moreover only be utilized at increased temperatures in baths with high alkalinity, which significantly restricts the application capabilities with alkaline-sensitive coating materials. The baths known so far can therefore only be conditionally utilized for the copper deposition using resist techniques within conductor track technology.

Formaldehyde-free baths for the electroless deposition of copper are already known within prior art. These baths comprise nitrogen-containing substances. EDTP or EDTA (US 4,617,205), triethylene diamine (US 4,143,186) and polyalkylene polyamines (US 3,793,038) have already been described as nitrogen-containing substances of such baths.

It has been observed that prior art for the previously known copper baths for the electroless deposition entails the following disadvantages:

- a) the baths are strongly alkaline
- b) the quality of the copper coating must be improved
- c) the substances used are toxic.

The present invention addresses the problem of providing a formaldehyde-free bath for the electroless deposition of copper using a more environmentally friendly reducing agent operating in the acidic range (pH range from 3.0 to 6.9).

This problem is solved through the invented bath according to the patent claims, optionally using polyethylene imines of formula I



where

$n = 2, 3, 4$ ; preferably for  $n = 2$ , and

$x =$  a positive number, preferably  $x = 30 - 1.5000$ ,

or are derived from them;

and especially using polyethylene imines of the general formula II



where  $n$  and  $x$  have the same meaning as above and

$\text{Y}$ ,  $\text{Q}$  and  $\text{Z} =$  hydrogen, methyl, ethyl, propyl and/or butyl.

The most significant point of the present invention is that as the reducing agent formic acid or its derivatives can be used.

Formic acid is an inexpensive chemical product and is utilized, for example, in food technology as a preservative.

As the simplest carboxylic acid, it can also be viewed as an aldehyde and has, in fact, marked reductive properties. Thus, formic acid is capable of reducing silver and mercury ions in aqueous solution to metals.

In this connection there has been no lack of consideration and experiments to utilize it quite specifically also for copper reduction.

E. B. Saubestre describes for example in *Proc. Amer. Electroplaters Soc.* (1959), pp. 264-276 corresponding experiments with formic acid. As a result of this work is reported that the reduction of copper (II) is only successful to the copper (I) state and, when formate is added to the formalin bath, the quality of the copper coating is degraded.

U. Gehringer et al. describe in *Zeitschrift für Galvanotechnik* 80 (1989) p. 406 that autocatalytic deposition of copper is not possible in the presence of the reducing agent formic acid.

It could now unexpectedly be shown that by adding the complex formers according to claim 7, autocatalytic reduction of copper (II) ions with formic acid, preferably also on surfaces pretreated with palladium activators, can be achieved and that this process can be utilized for the deposition of copper in industrial engineering.

As reducing agents are suitable not only formic acid, but also its salts or its derivatives or addition compounds. As salts of formic acid should be listed, for example, such salts as those comprising elements of the first, second or third main group [of the periodic table], in particular lithium, sodium, potassium, magnesium, calcium, boron and aluminum. Furthermore, ammonium and copper formate are also utilizable. Suitable are also salts of formic acid comprising nitrogen-containing cations, for example quaternary ammonium compounds.

Derivatives of formic acid that can be utilized are formic acid esters and/or formic acid amides. Methyl, ethyl and propyl esters are to be especially emphasized.

According to patent claim 7, for the copper complexation the compounds listed in this claim can be drawn on. As complex formers are suitable carboxylic acids or their salts, hydroxycarboxylic acid or their salts, alcohols or alcoholates, phosphonic acids or their salts, primary, secondary or tertiary amines or polyamines, amino acids or their derivatives, polyethylene imines or their substitution products. Especially suitable are polyalkylene imines.

The polyethylene imines or their derivatives (for example disclosed in DE OS 37 43 744, US 4,121,8982 [sic]) have unexpectedly been found to be very good complex formers in the acidic, neutral and alkaline pH ranges. Therewith all known reducing agents which are generally suitable for electroless deposition can be utilized for the deposition of copper. In the deposition process the reduction of copper (II) ions to copper metal takes place.

Polyethylene imines are known large-scale industrial products; within the field of galvanotechnics they have already attained significance as brighteners in the deposition of gold-silver (DE OS 2413736); the same applies also to the electrodeposition of zinc.

Polyethylene imines are not uniform compounds. Rather, they are mixtures having highly different molecular weights. These mixtures are obtained through the polymerization of aziridine and substituted aziridines. It can be stated that the low-molecular-weight as well as also the high-molecular-weight, linear or branched, primary, secondary or tertiary types alone or in mixtures with other complex formers of other classes can be employed for reductive copper deposition.

It is optionally possible to utilize one complex former or a mixture of different complex formers in the baths according to the invention.

As stated in the examples, a mixture of copper complexes can advantageously be utilized, which is comprised of biologically readily degradable complex formers with functional -OH and

-COOH groups. These complex formers predominantly complex copper. The compounds listed in claim 7 can be added in quantities starting at 50 mg/L.

The copper coating solutions are of relatively simple composition and absolutely stable. Copper is instantaneously deposited in a bright lustrous salmon-red color onto the appropriately pretreated substrates without any initial deposition of dark dirty copper taking place. Since stabilizers are not required and no decomposition products of formic acid have any undesirable effects on the metal deposition, a highly pure copper deposition results.

If especially pure copper layers are to be deposited at low temperatures (ambient temperature to 50°C), it is advantageous to choose only nitrogen-containing complex formers, especially in order to conduct the process economically, and to carry out the bath regeneration with a copper formate solution.

The pH range between 3.0 and 6.9 claimed according to the invention in claim 12 has its optimal range between 4.0 and 6.0. For the pH adjustment formic acid or alkali hydroxides are utilized in order to exclude foreign ions from the bath.

The deposition temperature is in the range from 25°C up to 100°C, preferably from 70°C to 80°C.

The copper metallization can also be carried out in an autoclave; the deposition temperature is consequently above the boiling point of water.

If the corresponding contacting capabilities are available, according to claim 11 an electric potential can be applied or an AC voltage can be superposed to support the copper deposition. The requisite level of the potential is an empirical value and depends on the composition and geometry of the bath.

The regeneration of the bath systems described in the patent is extremely simple.

The copper can be added as copper salt solution, the apportioning taking place automatically via a photometer.

The pH adjustment can take place via a measuring electrode and is performed using formic acid, which simultaneously functions as reducing agent. Stabilizers are, as a rule, not required since the deposition systems involved here are stable systems.

With the invented formaldehyde-free acidic copper bath described, pure ductile copper coatings can be produced according to an extremely economical and environmentally friendly process.

Application of the invented baths is also feasible for the deposition of copper alloys. As mixtures of metal salts can be utilized, for example, sulfates, nitrates, oxides, hydroxides, carbonates or acetates of the metals copper, nickel, cobalt, iron or manganese. With the complex formers according to the invention these metallic compounds form complex compounds suitable for the deposition of copper or copper alloys.

Bath additives, for example, of nickel, cobalt, iron or manganese serve as true alloy metals and do not destabilize the reductive copper bath. When using phosphinic acid or its salts, phosphorus is also incorporated into the system as an alloy component. Therewith the application range of the deposited copper alloys is advantageously extended.

The following examples are intended to elucidate the invention:

#### EXAMPLE 1:

Copper sulfate pentahydrate	19.65 g/L
Ethylene diamine	10.40 g/L
Polyethylene imine	15.00 g/L
Lugalvan 35®, product of BASF	
Sodium formate	10.00 g/L

pH adjusted to pH 4.5 with formic acid; 50°C

EXAMPLE 2:

Copper sulfate pentahydrate	11.80 g/L
Diethylene triamine	11.00 g/L
Sodium formate	10.00 g/L
pH adjusted to 6.0 with formic acid; 70°C	

EXAMPLE 3:

Copper sulfate pentahydrate	19.65 g/L
Ethylene diamine	10.30 g/L
1-hydroxyethane-1, 1-diphosphonic acid	1.90 g/L
Sodium phosphate dodecane hydrate <sup>1</sup>	10.00 g/L
Sodium formate	15.00 g/L
pH adjusted to 6.0; 60°C	

EXAMPLE 4

Copper sulfate pentahydrate	19.65 g/L
Boric acid	20.00 g/L
Tartaric acid	15.50 g/L
Copper formate	0.01 g/L
Sodium formate	10.00 g/L
pH adjusted to 5.0; 60°C	

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<sup>1</sup> Probably dodecahydrate

#### EXAMPLE 5

Copper sulfate pentahydrate	19.65 g/L
Ethylene diamine	10.00 g/L
Succinic acid	20.25 g/L
Boric acid	10.00 g/L
Sodium formate	10.00 g/L
pH adjusted to 5.0; 50°C	

#### EXAMPLE 6

Copper sulfate pentahydrate	11.80 g/L
Succinic acid	12.50 g/L
Quadrol	10.00 g/L
Sodium phosphate dodecahydrate	5.00 g/L
Sodium formate	15.00 g/L
pH adjusted to 5.0; 70°C	

#### EXAMPLE 7

Copper sulfate pentahydrate	19.65 g/L
D-fructose	31.00 g/L
Citric acid	36.00 g/L
Sodium phosphate dodecahydrate	15.00 g/L



Sodium formate	10.00 g/L
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pH adjusted to 6.0; 70°C

#### EXAMPLE 8

Copper sulfate pentahydrate	19.65 g/L
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Sodium glucomate	37.00 g/L
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Polymin P (Polyethylene imine)	5.00 g/L
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Sodium diphosphate pentahydrate	15.00 g/L
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Sodium phosphate dodecahydrate	15.00 g/L
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Sodium formate	15.00 g/L
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pH adjusted to 5.0; ambient temperature

#### EXAMPLE 9

Copper sulfate pentahydrate	19.65 g/L
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Sodium acetate trihydrate	42.00 g/L
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Sodium diphosphate pentahydrate	35.00 g/L
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Sodium formate	20.00 g/L
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pH adjusted to 6.90; 50°C

#### EXAMPLE 10

Copper sulfate pentahydrate	19.65 g/L
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Glycerin	15.80 g/L
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Sodium diphosphate pentahydrate	34.00 g/L
Sodium formate	20.00 g/L
pH adjusted to 6.0; 70°C	

#### EXAMPLE 11

Copper sulfate pentahydrate	19.65 g/L
Glycerin	23.40 g/L
Sodium diphosphate decahydrate	20.00 g/L
Sodium phosphate dodecahydrate	25.00 g/L
Sodium formate	15.00 g/L
pH adjusted to 6.0; 80°C	

#### EXAMPLE 12

Copper sulfate pentahydrate	19.65 g/L
Iminodiacetic acid	41.50 g/L
Sodium phosphate dodecahydrate	5.00 g/L
Sodium formate	20.00 g/L
pH adjusted to 6.0; 80°C	

#### EXAMPLE 13

Copper sulfate pentahydrate	19.65 g/L
Ethylene diamine	18.70 g/L

pH adjusted to 5.0 with formic acid; 90°C

#### EXAMPLE 14

Copper formate	0.075 M
Polyimine G 35	20.00 g/L
Diethylene triamine	0.025 M
Sodium hydrogenphosphate	0.05 M
Sodium dodecylether phosphate	10 mg/L

pH adjusted to 6.5; 90°C

#### EXAMPLE 15

Copper formate	11.5 g/L
Pentaethylene hexamine	36.0 g/L
Sodium diphosphate decahydrate	20.0 g/[L]
Sodium phosphate dodecahydrate	25.0 g/L
Sodium formate	15.0 g/L

pH adjusted to 6.0; 80°C

#### EXAMPLE 16

Copper sulfate pentahydrate	19.65 g/L
Ethylene diamine	10.40 g/L
Polyethylene imine	15.00 g/L

Sodium formate	10.00 g/L
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pH adjusted to 4.5; 80°C

#### EXAMPLE 17

Copper sulfate pentahydrate	19.65 g/L
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Pentaethylene hexamine	33.60 g/L
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1-Hydroxyethane diphosphoric acid	1.50 g/L
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Sodium formate	12.00 g/L
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pH adjusted to 5.0 with formic acid; 75°C

#### EXAMPLE 18

Copper sulfate pentahydrate	19.65 g/L
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2-Aminopropane	4.50 g/L
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Polyimine G 35	14.40 g/L
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Sodium formate	12.00 g/L
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pH adjusted to 4.0 with formic acid; 75°C

## Patent Claims

1. Formaldehyde-free bath for the electroless deposition of copper with a copper salt, a complex former or a mixture of several complex formers and a reducing agent, characterized in that it comprises formic acid or its salts or addition compounds as a reducing agent or as a mixture of reducing agents.
2. Bath as claimed in claim 1, characterized in that it comprises copper formate and a complex former or a mixture of several complex formers and optionally additives.
3. Bath as claimed in claim 1, characterized in that it comprises as a salt of formic acid such of the elements of the first, second or third main group of the periodic system of elements.
4. Bath as claimed in claim 1, characterized in that it comprises salts of formic acid with nitrogen-containing cations, such as ammonium formate.
5. Bath as claimed in claim 1, characterized in that it comprises activated formic acid as the addition compound of formic acid.
6. Bath as claimed in claim 1, characterized in that it comprises formic acid ester or formic acid amides as reducing agents.

7. Bath as claimed in claims 1 or 2, characterized in that it comprises as complex formers carboxylic acids or their salts, hydroxycarboxylic acids or their salts, alcohols or alcoholates, phosphonic acids or their salts, primary, secondary or tertiary amines or polyamines, amino acids or their derivatives, polyethylene imines or their substitution products.
8. Bath as claimed in claim 7, characterized in that the complex formers to be added are present in the bath at a concentration of 0.05 - 100.00 g/L.
9. Bath as claimed in claim 2, characterized in that it comprises maleic acid, succinimide, phosphates, fluorides, chlorides, bromides or diphosphates as additives.
10. Method for the deposition of copper using the baths as claimed in at least one of claims 1-9, characterized in that for the support of the autocatalytic deposition a laser beam is utilized.
11. Method for the deposition of copper using the baths as claimed in at least one of claims 1-9, characterized in that for the deposition of copper an electric potential is applied or an AC voltage is superposed.
12. Method as claimed in claim 10, characterized in that the copper deposition is carried out in a pH range of 3.0 to 6.9.
13. Method as claimed in claim 10, characterized in that the deposition temperature is maintained in the range from 25°C to 100°C.

14. Method as claimed in claim 10, characterized in that the copper deposition is carried out at a deposition temperature greater than 100°C in an autoclave.

15. Method as claimed in claim 10, characterized in that for the copper regeneration in the bath copper is anodically dissolved via a diaphragm system.

16. Use of polyethylene imines having the general formula I



where

$n = 2, 3, 4$  and

$x = 30 - 1.500$

as content substance(s) in aqueous formaldehyde-free baths for the chemical deposition of copper or copper alloy.

17. Use of polyethylene imines having the general formula II



where

$n = 2, 3, 4$

$x = 30 - 1.5000$ , and

Y, Q and Z = hydrogen, methyl, ethyl, propyl and/or butyl, as content substance(s) in aqueous formaldehyde-free baths for the chemical deposition of copper or copper alloy.